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Chemical interaction of well composite samples with supercritical CO_2 along the cement - sandstone interface

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Abstract

Chemical interaction of Portland cement with supercritical CO_2 along the cement - sandstone interface was investigated. To model a well in a CO_2 geological storage site, we prepared the well composite sample consisting of casing, Portland cement and sandstone. Using this sample, we conducted batch experiments in a laboratory scale to estimate the chemical interactions of CO_2 under a reservoir condition (10MPa, 50˚C, 0.5M NaCl). The elemental and crystal phase analysis of CO_2 exposed samples were carried out by SEM-EDS and μ-XRD. In the cement region, a carbonation zone of the cement occurred adjacent to the sandstone with both samples exposed to CO_2. From the results of SEM-EDS analysis, it was found that Ca concentration in the carbonation zone increased about 20% in comparison to that in the unaltered cement zone while concentration of Mg, Si, S at the carbonation zone decreased. Crystal phase at the carbonation zone were predominantly $CaCO_3$ (calcite, aragonite and vaterite) and trace Friedel's salt. In addition, $CaCO_3$ were sparsely precipitated in the pore spaces of sandstone along the sandstone-cement interface. These results indicate that the formation of carbonation layer provides as an effective barrier to further CO_2 attack.

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Keywords: well integrity, Portland cement, well composite sample, chemical interaction of CO_2, SEM-EDS, μ-XRD, carbonation

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1. Introduction

Well integrity is one of the most important issues for the safety of CO_2 sequestration into the subsurface. A typical CO_2 injection well is constructed with steel casing pipe and cement. It can be incorporated into standard primary cementing operations for zonal isolation of CO_2 injection well. The cement is placed in the annulus between casing and rock to support casing and prevent vertical fluid migration. After the CO_2 injection period, well plugging operation is performed for well abandonment. The well abandonment typically requires the sealing with cement plugs inside the casing from the reservoir to the caprock.

At the abandoned well, there are six possible leakage pathways of CO_2 [1]. These leakage pathways are caused by the decline of the sealing property of the cementing and by the degradation of the well materials as a result of the chemical interaction with CO_2. During the CO_2 injection period, operators can perform the periodic well logging for the well integrity, and also take a remedial action depending on the logging results. However, after the well-closing, it will be difficult to observe the state of the well by well logging. The injection wells must have wellbore integrity to ensure that there is no CO_2 leakage during the injection period, as well as during the long-term period for over 1,000 years.

In order to evaluate the long-term integrity of the abandoned wells in CO_2 sequestration, it is essential to understand the geochemical interaction between CO_2 and well materials. The potential effects of CO_2 on cement are varied and depend strongly on the extent of carbonation. Various studies of geochemical interaction between CO_2-saturated fluid and well cement were investigated in the lab-scale and field-scale experiments [2-7]. However, in previous reports, there is difference in the interpretation of cement durability because of uncertainties about the nature and extent of CO_2-saturated fluid interaction with the cement. One of the reasons is that most experiments in laboratory only considered the interaction between CO_2 and cement.

In this study, we focuses on the well cement interaction with supercritical CO_2, and the lab-scale study with on the cement interactions for the well integrity. Our investigation to improve understanding of a near wellbore system, we prepared well composite samples consisting of carbon steel casing, Portland cement, and berea sandstone. Using the samples, batch experiment was conducted under a reservoir condition in order to examine chemical reactions in the steel-cement-formation composite without CO_2 flow. The well composite samples were exposed with a water-saturated supercritical CO_2 (wet-CO_2) and a CO_2 saturated brine for 56 days.

2. Methodology

2.1. Preparation of well composite samples

Fig.1 shows a schematic diagram of well composite sample. The samples were prepared by cylindrical sandstone, 30 mm in diameter and 50 mm high. To model a well in geological formation, a 4 mm in diameter steel casing (J55) was embedded and fixed with Portland cement corresponding to API 10B Class A (water/cement ratio: 0.46) in a hole, 13 mm in diameter and 40 mm deep, made in the centre of a sandstone sample. The sandstone type was selected in berea sandstone, which is quartz-rich sandstone and has a homogeneous pore structure. Table 1 lists chemical and crystal compositions of the casing, Portland cement and sandstone.

2.2. Batch experiment

Batch experiment of the samples with supercritical CO_2 was performed at 50˚C and 10 MPa of CO_2 pressure corresponding roughly 1 km below the ground surface. Fig.2 shows the schematic of the batch experimental setup. Two well composite samples were piled in a pressure vessel (63.5 mm in inner diameter and 200 mm in depth) filled to approximately half-full with 0.5M NaCl solution (brine). Subsequently, the vessel was vacuumed to remove the remaining air. CO_2 gas was added to the vessel and exposed to the samples for 56 days under the condition of 50˚C and 10 MPa in which CO_2 was in a supercritical state. During the batch experiment, the upper sample was exposed to a water-saturated supercritical CO_2 phase (called as wet-CO_2) while the bottom sample reacted with a CO_2

saturated brine phase. After the batch experiment, CO_2 reacted samples were longitudinally halved and polished to the cross section by 6000 mesh SiC abrasive powder for elemental and crystalline phase analysis.

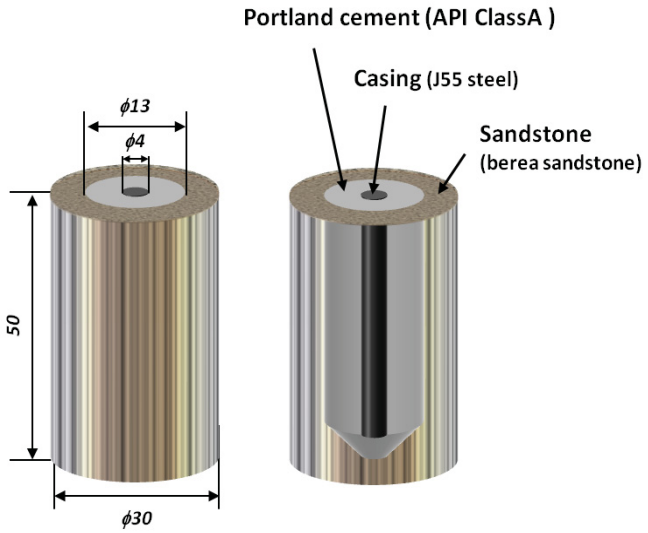

Fig. 1. Schematic diagrams of well composite sample.

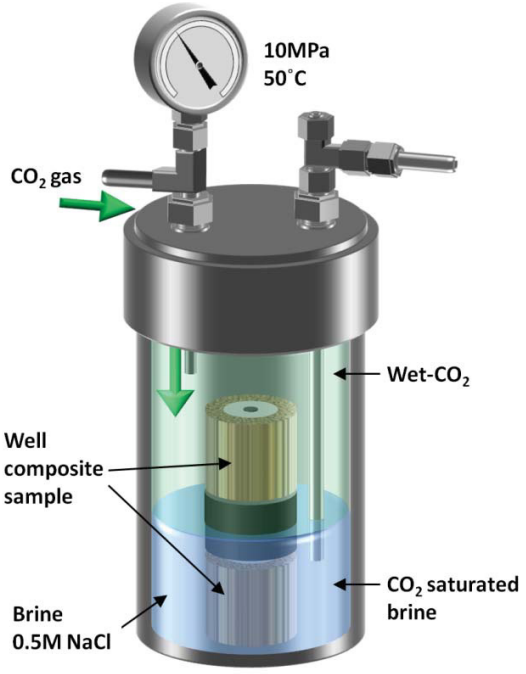

Fig. 2 Schematic diagram of the batch experimental setup

Table 1 (a). Chemical compositions (in wt%) of the steel casing (J55 , Portland cement and Berea sandstone calculated by SEM-EDS analysis.

Component	Casing (J55)	Portland cement	Berea sandstone
Na_2O	-	1.5	0.8
MgO	-	1.3	0.4
Al_2O_3	-	7.2	2.3
SiO_2	0.6	25.3	95.1
SO_3	-	2.0	-
K_2O	-	1.0	0.5
CaO	-	58.5	0.3
TiO_2	-	0.26	0.2
MnO	1.4	-	-
FeO	98.0	2.3	0.2
Cl	-	-	0.1

Table 1 (b). Crystal compositions (in wt%) of the casing, Portland cement and sandstone calculated by XRD analysis.

Crystal phase	Chemical formula	Casing (J55)	Portland cement	Berea sandstone
Brownmillerite	Ca_2FeAlO_5	Not analyzed	33	-
Katoite	$Ca_3(Al(OH)_6)_2$		35	-
Portlandite	$Ca(OH)_2$		11	-
Nonacalcium cyclo-hexaaluminate	$Ca_9(Al_2O_6)_3$		6.0	-
Gypsum	$CaSO_4 \cdot H_2O$		3.0	-
Hatrurite (Alite)	$Ca_3(SiO_4)O$		3.0	-
Periclase	MgO		8.0	-
Quartz	SiO_2		-	94
Microcline	$K\ (AlSi_3O_8)$		-	2.5
Clinochlore	$(Mg_{11.148}Fe_{0.852})((Si_{4.99}Al_{3.01})O_{20}(OH)_{16})$		-	1.5
Muscovite	$KAl_{2.20}(Si_3Al)_{0.975}O_{10}\ ((OH)_{1.72}O_{0.28})$		-	2.1

2.3. Analytical procedure

The observation and elemental analyses of the CO_2 exposed samples were carried out by an SEM-EDS: a SEM was VE-9800 (KEYENCE Corporation) and an EDS was INCA energy system equipped with an Si(Li) semiconductor detector [PENTA FETx3 (Oxford Instruments), sensitive area: 30mm^2, energy resolution: <133eV@MnKα]. The SEM observation and EDS analysis were operated at an acceleration voltage of 20 kV and a beam current of 0.3 nA. The quantitative procedures of the matrix correction method used in the EDS system.

An X-ray diffractometer (SmartLab, Rigaku Corporation) equipped with a 9 kW rotating anode (Cu) x-ray generator (operated at 45 kV and 200 mA) and a high speed 1D detector was used for crystalline phase analysis in a micro area of the reacted samples. For the nondestructive μ-XRD analysis, a polycapillary x-ray focusing optics (named as CBO-f unit) and a parabolic multilayer mirror optics (named as CBO unit) was incorporated with the XRD spectrometer. These units enable to focus the brilliant x-rays to ϕ0.4 mm at the focal point on the sample surface.

3. Results and Discussions

3.1. Observation of well composite samples after CO_2 exposure

After CO_2 exposure for 56 days, cement alterations were clearly observed along the cement-sandstone interface under CO_2 saturated brine condition and wet-CO_2 condition. The cement alteration zone was visibly divided into two layers; one is an orange-colored layer (carbonation zone) in the outer cement, and another is white-colored layer in the inner cement. The carbonation zone of the cement occurred adjacent to the sandstone after exposure to both CO_2 conditions. The carbonation depth under wet-CO_2 condition was larger than that under CO_2-saturated brine condition. However, the carbonation depth was a few millimeters and inner part of cement did not altered within 56 days of the reaction. This indicates that the sandstone surrounding the cement serves as a buffer for CO_2 attack. Based on the results the predicted 30 years carbonation depth evaluated by a logarithmic approximation was estimated at 4.5 mm for wet-CO_2 condition and 0.76 mm for CO_2-saturated brine condition, respectively [8]. In addition, the alteration of steel casing was limited on the both conditions.

3.2. SEM-EDS and μ-XRD analysis at carbonation cement

SEM-EDS maps of Ca of well composite samples exposed to wet-CO_2 condition (a) and CO_2-saturated brine condition (b) at the cement-sandstone interface are shown in Fig. 3. In addition, Fig. 4 shows the quantitative results of Na, Mg, Al, Si, S, Cl, Ca and Fe at the carbonation zone and unaltered zone calculated by SEM-EDS. From these results of SEM-EDS analysis, it was found that Ca concentration at the carbonation zone increased 10% - 20% in comparison to that in the unaltered cement zone while concentration of Mg, Si, S at the carbonation zone decreased.

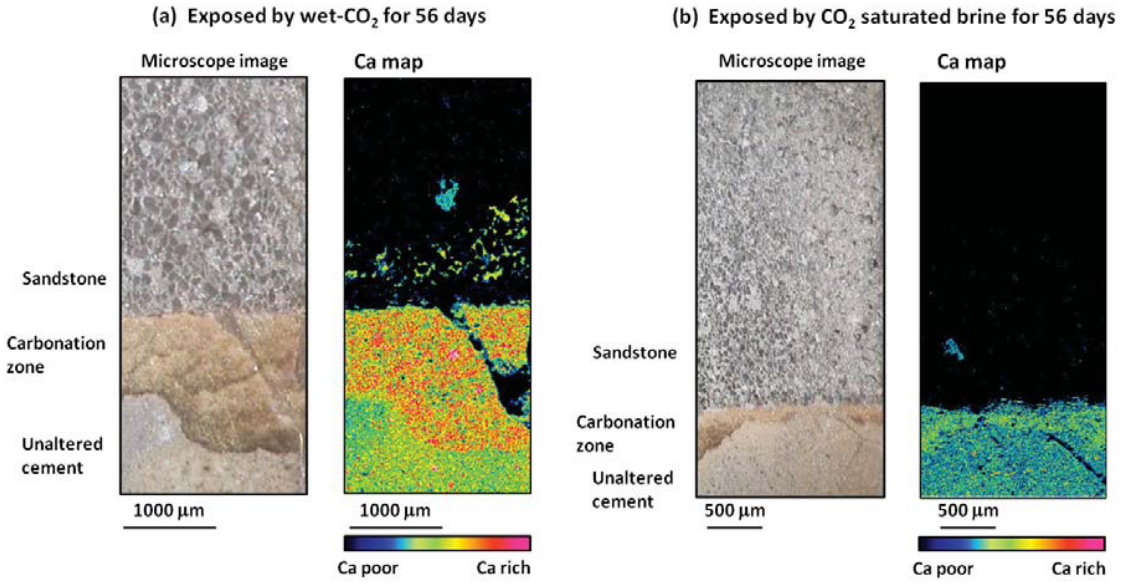

Fig. 3. Optical microscope image and SEM-EDS map of Ca of well composite sample (berea sandstone) exposed to wet-CO_2 for 56 days (a) and CO_2 saturated brine for 56 days (b) at the cement-sandstone interface.

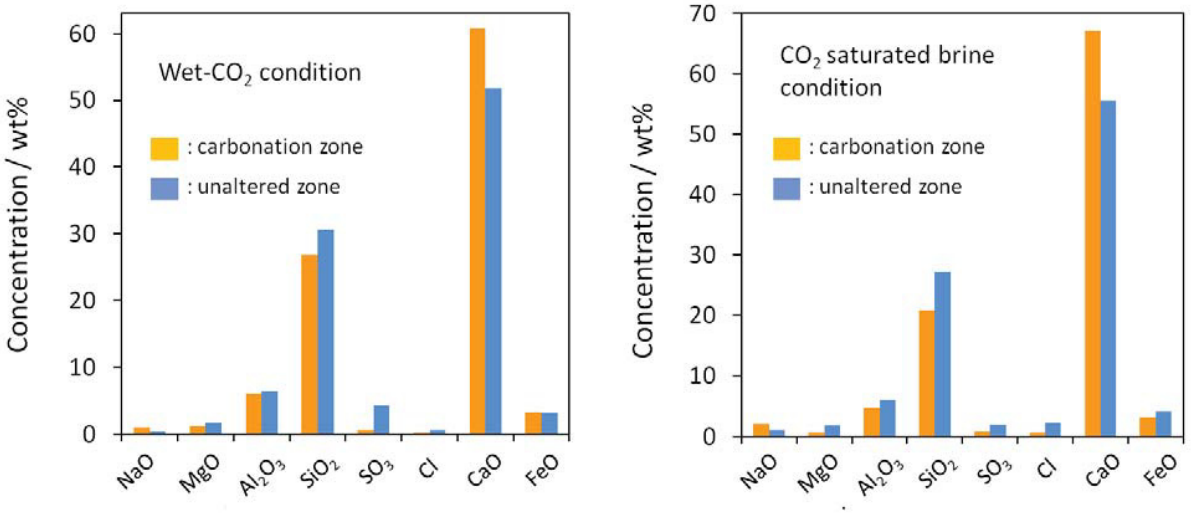

Fig. 4. Quantitative results of Na, Mg, Al, Si, S, Cl, Ca and Fe at carbonation zone and unaltered zone under CO_2 saturated brine condition and wet-CO_2 condition analyzed by SEM-EDS.

Table 2 lists the μ-XRD results at the carbonation zone of well composite samples exposed to wet-CO_2 and CO_2-saturated brine condition. Crystal phase at the carbonation zone were predominantly $CaCO_3$ (calcite, aragonite and vaterite) and trace Friedel's salt. Three polymorphs of $CaCO_3$ (calcite, aragonite, and vaterite) were identified in the carbonation zone. Aragonite and vaterite are both metastable relative to calcite, in particular, vaterite is very rare in nature, but it is often reported in other studies of cement carbonation [7, 9]. The polymorphic crystallization of $CaCO_3$ is effect of inorganic ions and pH condition in the reaction field [10]. Magnesium ions in the mother solution favors aragonite formation very strongly while NaCl inhibited aragonite formation. In contrast, high pH condition in cement favors vaterite and calcite formation. In addition, vaterite is precipitated from C-S-H (calcium silicate hydrate) and not from portlandite in cement [11].

Table 2. Quantitative results of μ-XRD analysis (in wt. %) at the carbonation zone of well composite samples

Crystal phase	Chemical formula	Wet-CO_2	CO_2 saturated brine
Calcite	$CaCO_3$	47	64
Aragonite	$CaCO_3$	36	20
Vaterite	$CaCO_3$	14	0.9
Friedel's salt	$3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10\ H_2O$	3	-
Calcio-olivine	Ca_2SiO_4	Trace	Trace
Quartz	SiO_2	-	15

Fig. 5 shows two colored maps by SEM-EDS of Ca (red) and Si (green) along the cement - sandstone interface of the well composited sample exposed to wet-CO_2 condition. It was found that small Ca rich points were distributed in the pore spaces of sandstone along the sandstone-cement interface as shown in Fig. 5. Similar result was also reported by Kunieda et al [12]. This suggests that the calcium carbonate precipitation is a result of Ca^{2+} diffusion out of the cement coupled with inward diffusion of carbonated ion.

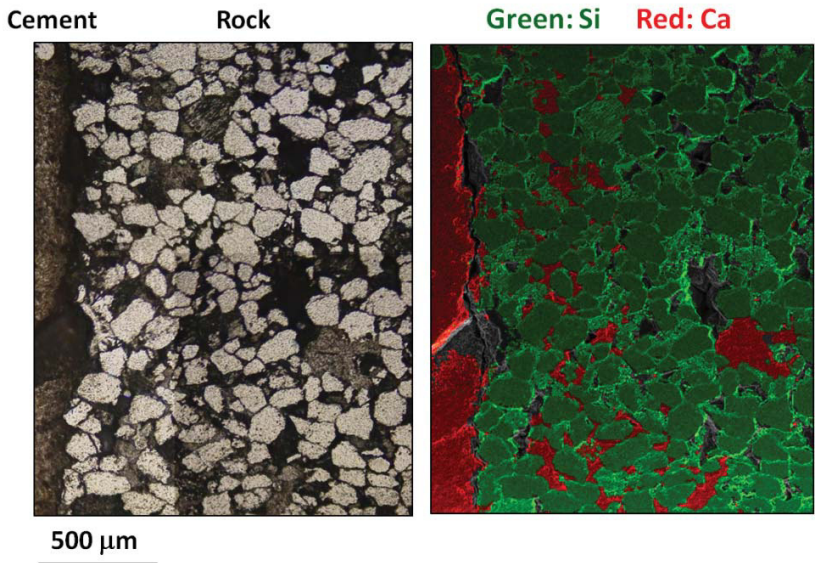

Fig. 5. Optical microscope image (left) and two colored maps by SEM-EDS (right) of Ca (red) and Si (green) along the cement - sandstone interface of the well composite sample exposed to wet-CO_2 for 56 days.

4. Conclusions

We performed batch experiment using well composite samples consisting of steel casing, Portland cement, and berea sandstone in order to understand the geochemical interaction of Portland cement with supercritical CO_2 along the cement - sandstone interface. From the batch experimental results, chemical interaction between CO_2 and Portland cement along the cement - sandstone interface in the wellbore is estimated as follows and as shown in Fig.6. The first step is the cement degradation due to cement hydration and dissolution of $Ca(OH)_2$ in the inner zone when brine or CO_2 penetrates into the cement. The cement hydration takes place regardless of CO_2 existence. The inner zone is showed a slight increase in porosity, resulting from the dissolution of $Ca(OH)_2$. And minerals released from cement fills up the pore space of sandstone along the cement - sandstone interface. The second step is formation and precipitation of fine $CaCO_3$ at the outer cement and in the pore spaces of sandstone. The formation of $CaCO_3$ decreases cement permeability and increases its compressive strength. Our experimental result in elsewhere [5] indicates that these chemical reactions along the cement–rock interface are begin immediately after the reaching CO_2 fluid to cement surface. These results indicate that the formation of fine carbonate provides as an effective barrier to further CO_2 attack.

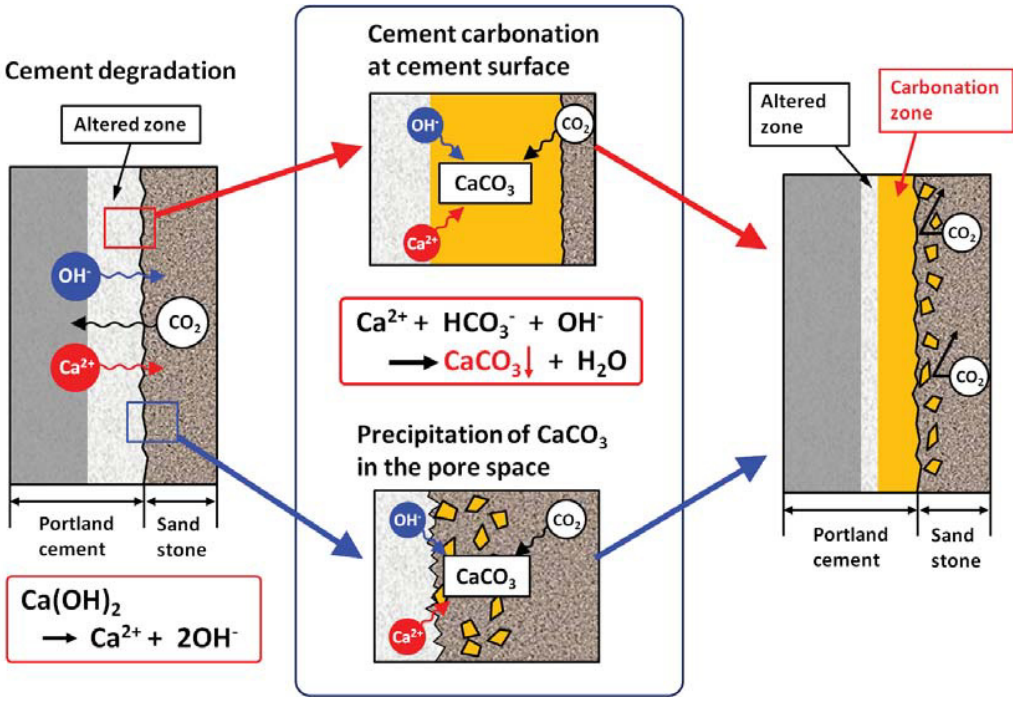

Fig. 6. Illustration of the chemical interaction between CO_2-saturated fluid and Portland cement along the cement - sandstone interface.

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